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An advanced OMVPE process is being developed for the deposition of III-V semiconductor materials and structures. There are important optoelectronic device structures which can not be realized by conventional means. The new OMVPE apparatus combines the multichamber reaction cell with deep UV photo-assisted growth and modulation flow epitaxial techniques. Using a combination of such processes, the growth temperature requirements for III-V alloys can be substantially reduced. Selective growth on a sub-micron scale will be attempted with in-situ interference holography. The materials and techniques developed in this research program will result in significant simplifications to the fabrication sequence required to realize complex integrated optoelectronic circuits.

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Table of Contents

I. Introduction

The Cornell OMVPE facility has been operational since December 1991. While rapid progress is being made towards the completion of the SDIO system, the multichamber apparatus (originally donated by General Electric and subsequently rebuilt) has been operational since January 1992. Since that time, research efforts have focused primarily on basic material studies of the AlGaAs and GaInP systems using Flow Modulation Epitaxy (FME). In the past year, significant advances have been made in exploring the advantages of FME. Using FME in a multichamber reaction cell configuration, we have been able to: produce high purity GaAs at unity V/III ratio, identify the effects of gas phase reactions of trimethylamine alane on AlGaAs film quality, and produce coherent ordered GaInP films on GaAs. In addition to our growth studies, efforts have been made to use α-carbon films as an lift-off mask for focused laser ablation patterning and subsequent regrowth.

The work unit consists of the principle investigator, 3 Ph.D. candidates and a Masters of Engineering candidate. This program also partially supports a research support specialist responsible for the OMVPE reactor construction.

II. Progress in the Past Year

The progress in the last year of this program has been highlighted below and appears in 6 sections. The first 2 sections are meant to give a brief update on the new facilities which supports compound semiconductor research activities at Cornell. Finally, the research focusing on basic growth studies and the use of α-carbon as an selective epitaxial mask will be discussed.

Organometallic Vapor Phase Epitaxy Facility

From January 1992 until now, various iterations have been made to optimize the safety features of the facility. The incineration/wet scrubbing system has been modified to accommodate the necessary arsine and phosphine flows. Strict lab policies and increased security provided by Cornell public safety have been instituted to provide a safer environment. Our characterization capability has been improved by the addition of a double crystal X-ray diffractometer. Installed in December 1992, this apparatus has become an integral part of our research program, particularly in the area of coherent ordered GaInP. Finally, a LPCVD system is currently on line for deposition of thin SiON dielectric films.

Reactor Design & Construction

Initial experiments on the SDIO reactor is expected to begin July 1993. The majority of the components (gas handling, electronics, computer interfacing, excimer pumped dye laser system) are completed leaving only the reaction cell to be finished. In addition to the completion of the reaction cell, the gas handling unit is being leaked checked and software is developed to computer automate the system. While construction is in its final stages, efforts are already underway to achieve submicron focused laser spots.

Results from this work will be integrated into the in-situ direct writing of epitaxial films.

Low Hydride Consumption

One of the major disadvantages of hydride-based low pressure OMVPE has been the inefficient use of hydrides (i.e. arsine, phosphine) in the growth process. High purity material often requires large V/III molar ratios. This poses a potential safety problem due to the expulsion of excess hydride, and also the need to have large quantities of high pressure toxic hydride cylinders on site. Using arsine and triethylgallium with flow modulation, a process has been developed that produces high purity GaAs using V/III ratios near unity. We have estimated an arsine incorporation efficiency exceeding 30%. This process greatly reduces the environmental impact and life safety risk of the hydride based OMVPE method.

All films were grown using FME at reduced pressures (76 torr). The substrates are rotated through group III rich and group V spatially rich zones without valve switching. During the group III exposure cycle the local V/III ratio is estimated to be 25% of the average value. The arsine flow requirements for obtaining good morphology has also been determined over a wide range of growth temperatures. When the substrate temperature is beyond 610 °C, good morphology can be attained using minimal arsine flows (V/III ratio of unity). Below 610 °C, more arsine must be supplied due to inefficient pyrolysis of the arsine.

The electrical quality of the films were assessed using room temperature and 77 K Hall measurements. The impurity concentration and low temperature (77 K) mobility for samples grown at 635 °C with V/III ratios from 1.8 to 22 are given in Figure 1. The net impurity concentration($N_d - N_a$) varied from $3.7(10^{14})$ to $6.9(10^{14})$ cm^{-3} while the total impurity concentration ($N_d + N_a$) varied from $7.7(10^{14})$ to $2.0(10^{15})$ cm^{-3}. The 77 K mobility varied from 55,000 to 110,000 cm^2/V s, with the maximum value obtained at V/III ratio of 5. A V/III ratio (an arsine efficiency of 17.2%.) of 1.8 resulted in a 77 K mobility of 93,000 cm^2/V s. The highest room-temperature mobility was greater than 8000 cm^2/V s.

Low temperature PL spectra of samples grown at 635 °C revealed dominant features in the excitonic region of the spectra is that of the neutral donor exciton (D°,X) for V/III ratios greater than 1.8. The neutral acceptor exciton peak (A°,X) is negligible in samples grown with V/III greater than 1.8, indicating strongly n-type material. Two acceptor peaks are noticed at V/III ratios of 1.8 or less. Using variable temperature PL, the one of the peaks (at 1.493 eV) is assigned to free to bound transition (e,A^0) of Mg. In addition, the other peak (at 1.489 eV) has been identified as a donor to acceptor transition of Mg. These results are consistent with other PL of OMVPE grown GaAs using TEG and arsine. Normal excitonic features were completely absent for material grown at sub-unity V/III. In addition, new features much weaker in intensity are possible due to defect related exciton emission at photon energies near 1.503 eV. Films grown at sub-unity V/III ratios also exhibited poor surfaces and reduced growth rate, indicative of

arsenic diffusion limited growth.

Gas Phase Reaction of Trimethylamine Alane

Trimethylamine alane (TMAA) has recently received much attention as a viable alternative aluminum source to the widely used trimethylaluminum (TMA). Using TMAA, TEG and arsine, under the appropriate growth conditions (high V/III ratios and gas velocities), can result in the highest purity OMVPE grown AlGaAs. This is believed to be due to a lack of direct aluminum-carbon bond in TMAA and also its ability to form involatile Al-O compounds when reacted with oxygen and H_2O, resulting in reduced oxygen contamination. TMAA has two major drawbacks. It has a low thermal decomposition temperature, allowing predeposition on the side walls of the reaction cell. Secondly, TMAA reacts strongly with conventional Ga sources (TMG or TEG) at room temperature. We have investigated the effects of gas phase reactions between TMAA, TEG and arsine on AlGaAs film quality.

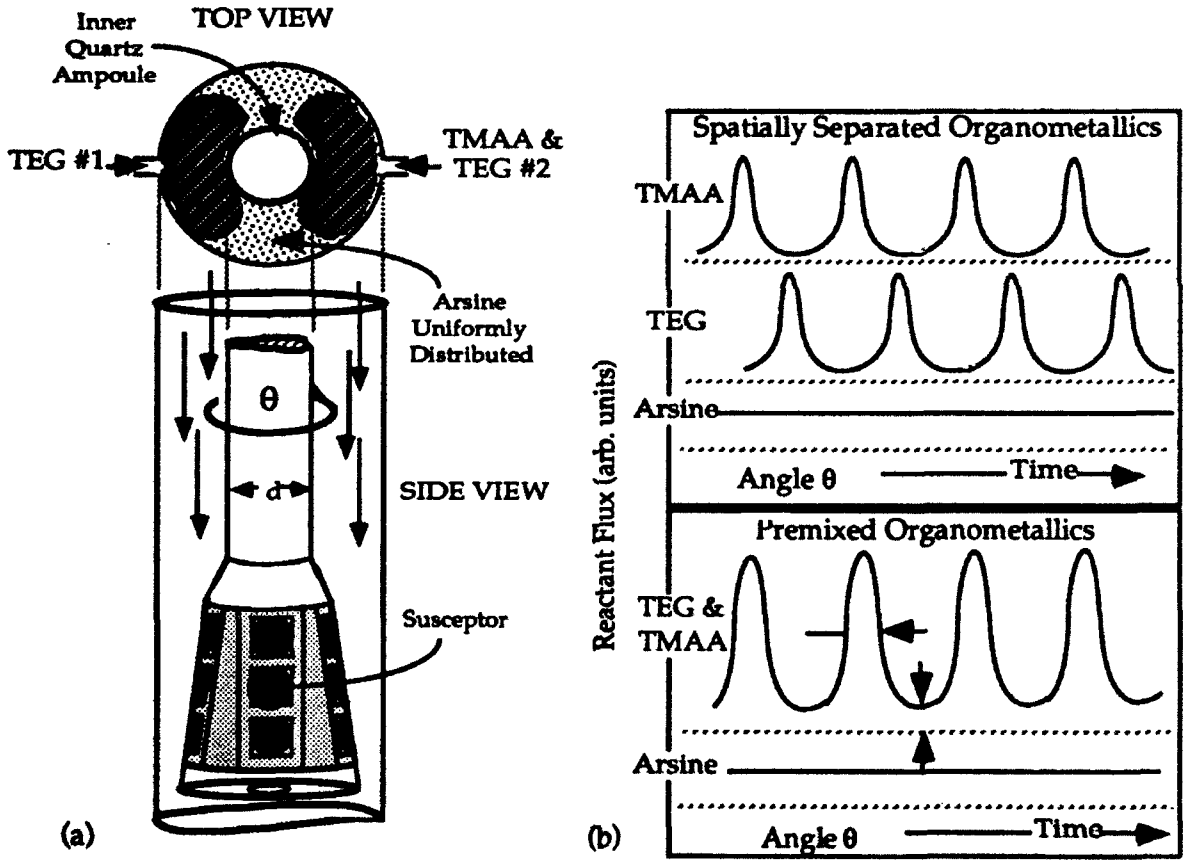

Figure 1. (a) Schematic illustration of implementation of flow modulation epitaxy in the multichamber cell. (b) The exposure cycle for premixed and spatially separated TMAA and TEG.

Two dominant effects were observed: one due to a TMAA-arsine reaction yields a strong influence of film composition with the V/III ratio, and the other resulting from TMAA-TEG which severely degrades thickness uniformity. The effects of each of these gas phase reactions in the upstream portion of the reaction cell were identified by spa-

tially separating TMAA and TEG in the gas phase using the multichamber reaction cell. Figure 1a illustrates the the flow modulation in the reaction cell. Figure 1b shows the exposure cycle for premixed and spatially separated TMAA and TEG. The arsine flow is uniformly distributed around the cell while the group III flux is localized and as a result modulated. The V/III ratio and growth temperature criteria for good surface morphology were investigated over the range from 635 to 750 °C. Good surface morphology was realized for a V/III ratio as low as unity over the entire temperature range. With growth temperature (670 °C) and group III flux constant the Al mole fraction was found to vary with V/III ratio in the conventional premixed growth mode. As shown in Figure 2a, more Al is incorporated in the film as the V/III ratio is decreased. The corresponding PL spectra, shown in Figure 2a inset, reveals the sample quality degrades with decreasing V/III ratio. The need for large arsine flows may imply that the TMAA-arsine reaction inhibits the TMAA-TEG reaction which is demonstrated to severely degrade the quality of the AlGaAs films.

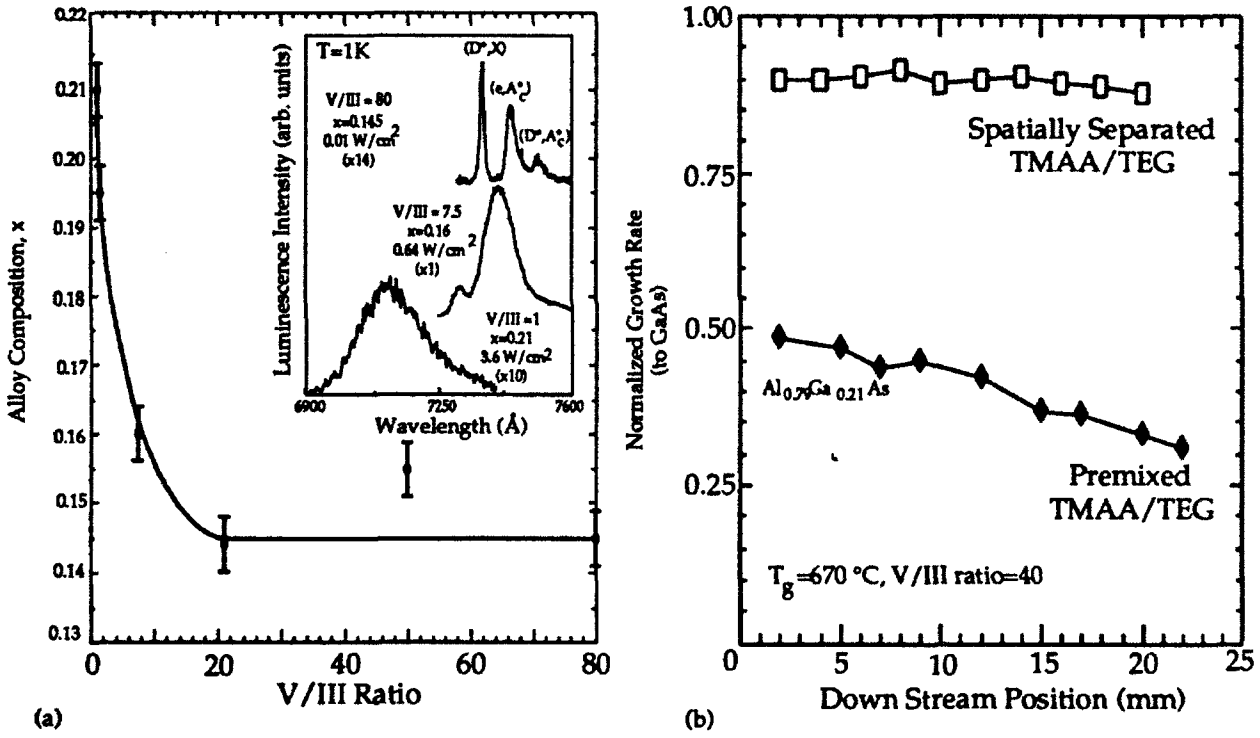

Figure 2. (a) Dependence of Al composition on V/III ratio for constant TEG and TMAA fluxes at 670°C . The inset is the corresponding low temperature PL for various V/III ratios. (b) The growth rate of AlGaAs downstream along the wafer when the TMAA and TEG are premixed prior to injection into the growth chamber and spatially separated in the gas phase.

Gas phase reactions between TEG and TMAA have major effects on the growth rate. When the TMAA and TEG are premixed, the AlGaAs growth rate is approximately half that of GaAs with same TEG reactant flux. A relatively high V/III ratio was used (V/III=80) to eliminate the effects of arsine flows described earlier. As shown in Figure 2b, the Al composition for AlGaAs grown using premixed sources was 79% whereas that for the spatially separated sources was nominally 40%. This is consistent

with fourier transform infrared studies on TMAA and TMG which report a depletion of Ga species in the gas phase. Color fringes were observed downstream along the wafer, indicating severe thickness nonuniformity (16% over a 20 mm diameter). In contrast, excellent thickness uniformity (1% over a 20 mm diameter) when the TEG and TMAA are separated in the vapor. The compositional uniformity was approximately the same (±2%) for both growth schemes, as was determined from X-ray rocking curve mapping. However, the material produced by premixing the reactants exhibited broad X-ray peak which is due to poor structural quality, as well as compositional grading. A comparison of PL spectra was made between layers grown by premixed and spatially separated growth modes for constant reactant flux. These experiments were performed at a growth temperature of 670 °C and a V/III ratio of 80. The material grown by with spatially separating the group III fluxes exhibits three order of magnitude higher PL intensity than the premixed grown material. A possible explanation for this effect is that volatile compounds are also present which participate in the growth process and incorporate non-radiative centers in the epitaxial layers. We have identified gas phase reactions of TMAA, TEG and arsine. Using the multichamber configuration, these gas phase reactions were minimized by spatially separating the reactants. As a result, high purity AlGaAs was produced using a substantially lower V/III ratio.

FME of AlGaInP Materials

The Flow Modulation Epitaxial growth of AlGaInP alloys and strained layer superlattices is of considerable interest for visible optoelectronic devices. Thus far we have established lattice matching conditions of both ordered (111 planes) and random GaInP alloys to GaAs. We can routinely produce GaInP films exhibiting low temperature (1K) PL linewidths less than 7 meV. However, X-ray data reveals that compositional grading is present in these layers. This effect is due to the erratic transport of trimethylindium (TMI). We have observed greater than 10 % flux variations of TMIn under constant carrier flow conditions over a 10 minute period. To alleviate this problem, an ultrasonic analyzer has been installed to monitor and regulate the TMI flow. Currently, a study is being conducted to determine the effects of ordering on lattice matching. We currently believe that the ordering produces significant strain relaxation which allows a broad alloy composition range ($\approx$ 15-20 %) of films to be deposited ($>$ 1 μm in thickness) without the presence of misfit dislocations. These coherent films exhibit large tetragonal distortions in the plane normal to the growth surface. Extending the lattice matching conditions is expected to have an important impact on devices produced from the AlGaInP and perhaps other In-containing material systems.

Selective Epitaxy Using α-Carbon Lift-Off Masks

As part of our efforts to investigate selective epitaxy, we are developing an in-situ process for patterning mask layers on a substrate just prior to regrowth. Our process employs a high power, pulsed laser, focused onto the surface of the masking layer. A very small area of the mask is actually ablated exposing the substrate below. The thickness of the mask layer and the number of laser pulses can be optimized to result in minimal damage to the substrate. The patterning step can be followed by a vapor

etch and/or an anneal to remove any residual substrate damage prior to growth.

The laser system we are using is a Lambda Physik tunable dye laser pumped by an excimer laser from the same manufacturer. The dye laser is operated at a wavelength of 480nm which is the peak of the tuning curve for the dye in use. The beam is then doubled in frequency using a BBO crystal. The output beam, at 240 nm and about 2 mW average power, is spatially filtered through a small bore, natural diamond pinhole and focused at the sample surface. Our final focussing lens is mounted on a motor driven stage that is translatable along three axes to 0.1 μm precision. Motion along the axis of the lens is used to focus the beam to the smallest possible spot, a few microns in diameter, while the other two axes are used to position the spot in the plane of the wafer surface. Patterns of a few square mm in size can be written without significant loss of focus.

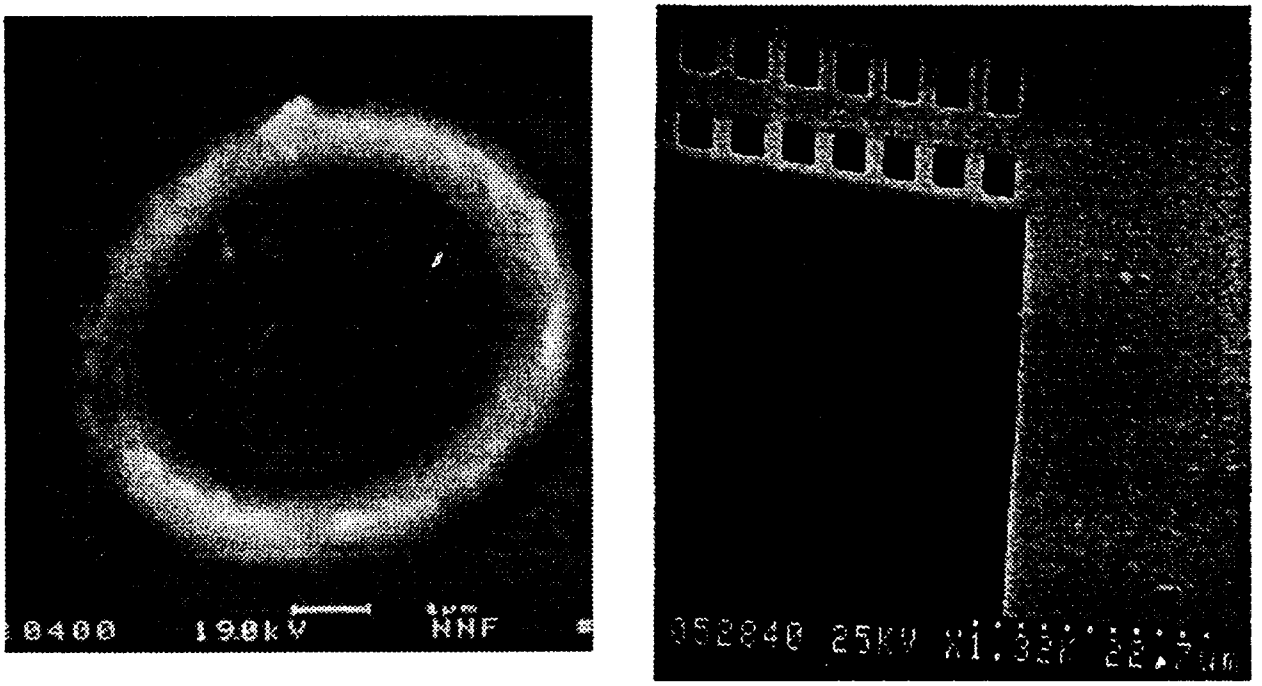

Figure 3. (a) Scanning electron micrograph of laser ablated spot patterned in carbon mask layer. The visible ring is a thermally generated ripple in the GaAs substrate surface. (b) Epitaxial lift off (AlGaAs) from a RIE patterned GaAs surface masked with carbon. The lighter region is the polycrystalline materials separated from the patterned substrate. Single cystal epitaxy is visible (darkest regions) in the patterned lines and squares.

So far we have been working with amorphous carbon layers as a epitaxial lift-off mask. These layers are deposited onto either Si or GaAs by an e-beam sublimation technique. The carbon layers have good adhesion to the substrate and are quite durable under growth conditions. We have also found that material that nucleates on the carbon mask during growth and lifts off provided that the single crystal epitaxy separates from the poly grown on top of the mask. This is illustrated in figure 3b. The mask itself is easily removed from the substrate by oxygen or hydrogen reactive ion etching (RIE). The

above all point to carbon as having good potential as a mask material for this process. It is interesting to note that the epitaxy grown on top of the carbon exhibits strong PL (from quantum well structures) and has reasonably good surface morphology.
We have investigated writing patterns in the carbon masks outside of the reactor and are about to begin growth experiments. As shown in Figure 3a, holes of about 5μm diameter have been patterned in carbon layers 0.5μm thick. Smaller holes will be feasible approaching the diffraction limit with customized UV optics. These wafers will be placed in the reactor and etched with HCl vapor. A structure consisting of alternating layers of GaAs and AlGaAs (marker layers to follow the growth front) will be grown. These will be studied by photoluminescence and scanning electron microscopy.

III. Publications

1. B.L. Pitts, D.T. Emerson, and J.R. Shealy,"Arsine Flow Requirement for the Flow Modulation Growth of High Purity GaAs using adduct-grade Triethylgallium," *Appl. Phys. Lett.*, **61** (1992), 2054-6.

2. B.L. Pitts, D.T. Emerson, and J.R. Shealy,"Gas Phase Reactions of Trimethylamine Alane in Low Pressure Organometallic Vapor Phase Epitaxy of AlGaAs , "*Appl. Phys. Lett.* , **62** (1993).

3. B.L. Pitts, D.T. Emerson, M. J. Matragrano, and J.R. Shealy,"Effects of Gas Phase Reactions of Trimethylamine Alane in Organometallic Vapor Phase Epitaxy Growth of AlGaAs,"submitted to *J. Crystal Growth*, (February 1993).

IV. Summary

In summary, during the 1992 reporting period we have nearly completed the selective growth reactor with the integral UV laser system, and we have pursued the Flow Modulation Epitaxial process for advanced III-V heterostructures. A low hydride consumption process was developed for both GaAs and AlGaAs films. The role of gas phase reactions with trimethylamine alane was clearly demonstrated using a unique multichamber reaction cell. During the investigation of In-containing alloys (GaInP on GaAs & GaInAs on InP), we have discovered that the conventional lattice matching wisdom does not apply when films are strongly ordered. A large range of alloy compositions has been identified with GaInP where lattice matching occurs in the plane of the growth while tetragonal distortion in the plane normal to the growth direction accommodates the misfit. Future studies of (001) ordered strained layer superlattices will likely offer new device structures containing coherent tetragonal III-V heterostructures. Finally, progress on selective epitaxy using a carbon lift-off mask was made. In conjunction with the laser ablation of this mask, a fully integrated in-situ selective growth process emerges which will potentially offer sub-micron resolution.